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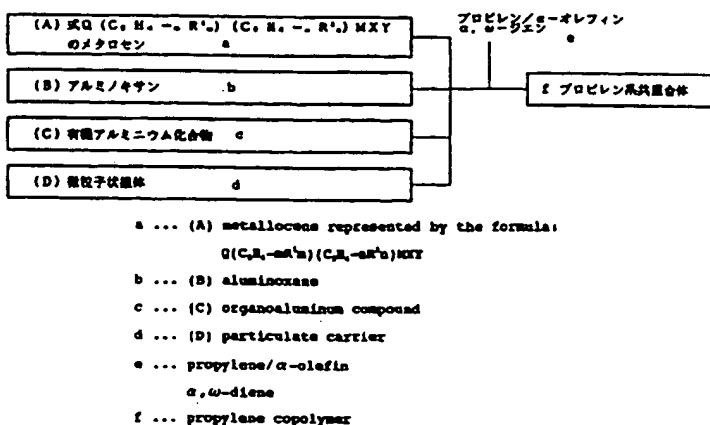
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(54) Title: PROPYLENE COPOLYMER AND PROCESS FOR THE PRODUCTION THEREOF

(54) 発明の名称 プロピレン系共重合体およびその製造方法



(57) Abstract

A propylene copolymer which exhibits high stereoregularity, is remarkably lowered in the non-stereoregular portion content of the copolymer, and has a narrow molecular weight distribution, high melt tension, excellent heat stability, a low MFR and excellent particle properties; and a process for the production thereof with a specific metallocene catalyst, which can be carried out even at a practical polymerization temperature. The process is characterized by copolymerizing propylene with an α , ω -diene by the use of a supported catalyst comprising the following compounds (A), (B), (C) and (D) as the main components at a temperature of 45 °C or above: compound (A): a specific metallocene represented by the formula: $Q(C_3H_4-mR^1)_n(C_3H_4-nR^2)_mMX$, compound (B): an aluminoxane, compound (C): an organoaluminum compound, and compound (D): a particulate carrier. The propylene copolymer is a highly stereoregular one characterized also in that the content of stereoirregular units formed by the 2,1-addition of propylene monomers based on all the propylene monomers introduced is regulated to be within a specific range.

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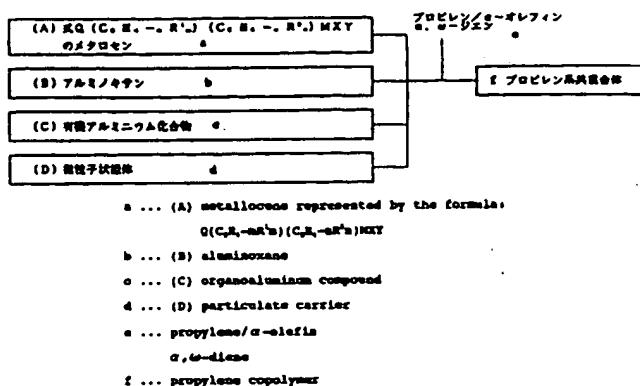
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Appended Disclosure Documents

International Search Report

(54) Title of the Invention

A PROPYLENE COPOLYMER AND A METHOD FOR ITS MANUFACTURE



(57) Abstract

A propylene copolymer and a method for its manufacture are provided using a specific metallocene catalyst, which copolymer has high stereoregularity at practical polymerization temperatures, whereby the quantity of heterogeneous bonds in the polymer is controlled to a high degree, which has a narrow molecular weight distribution, a high melt tension, heat stability, a low MFR and excellent particle properties.

It is characterized in that the propylene copolymer is manufactured by copolymerizing an α,ω -diene at a temperature of 45°C or higher using a supported catalyst system of which the principal components are compounds (A), (B), (C) and D as described below.

Compound (A): A specific metallocene as represented by $Q(C_5H_{4-m}R^1)^m(C_5H_4-R^2)^nMXY$

Compound (B): Aluminoxane

Compound C: An organoaluminum compound

Compound (D): A particulate carrier

A major characteristic of the propylene copolymer of this invention is that it is of high stereoregularity and that the proportion of units of irregular position based on 2-1 insertions of propylene monomers of all propylene insertions is regulated within a specific range.

A PROPYLENE COPOLYMER AND A METHOD FOR ITS MANUFACTURE

Technological Field

This invention relates to a propylene copolymer and to a method for its manufacture. In greater detail, it relates to a propylene copolymer and a method for its manufacture using a specific metallocene catalyst, which copolymer has high stereoregularity at practical polymerization temperatures, whereby the quantity of heterogeneous bonds in the polymer is controlled to a high degree, which has a narrow molecular weight distribution, a high melt tension, heat stability, a low MFR and excellent particle properties.

Prior art

Olefin polymers and copolymers such as polypropylene and polyethylene are widely used in various molding fields because they have superior mechanical properties and resistance to chemicals and because they are extremely useful in terms of balance with economic factors. These olefin polymers and copolymers are manufactured conventionally by polymerizing or copolymerizing olefins using so-called Ziegler-Natta catalysts in which transition metal catalyst components such as titanium trichloride, titanium tetrachloride or both substances supported on a carrier such as magnesium chloride are combined with an organoaluminum compound.

In recent years, olefin polymers or copolymers have been manufactured by polymerizing or copolymerizing olefins using catalytic systems different from conventional catalyst systems in that metallocene is combined with aluminoxane. Because olefin polymers or copolymers obtained using metallocene catalysts have narrow molecular weight distributions and because comonomers are uniformly copolymerized when they are copolymerized, the olefin polymers or copolymers that are obtained are characterized in being more homogeneous than those obtained conventionally. However the olefin polymers or copolymers obtained using these metallocene catalysts have lower melt tensions than olefin polymers or copolymers obtained using conventional catalyst systems and their uses are limited depending on the field of application.

Methods for increasing the melt tension and crystallization temperature of polypropylenes that have been disclosed include methods in which organic peroxides and auxiliary cross-linking agents are reacted with polypropylenes in a fused state (Japanese Patent Application Early Disclosure No. 59-93711 [1994] and Japanese Patent Application Early Disclosure No. 61-152754 [1986]) and methods in which polypropylenes having free terminal long chain branches and not containing gel are manufactured by reacting low decomposition temperature peroxides with semicrystalline polypropylenes in the presence of oxygen (Japanese Patent Application Early Disclosure No. 2-298536 [1990]).

Another method that has been proposed for improving melt viscosity properties such as melt tension is a method in which a composition in which polyethylene or polypropylene of different intrinsic viscosities or molecular weights are compounded and manufacture is effected by multiple stage polymerization of such compositions.

Examples of such methods include, for example, a method in which 2 to 30 parts by weight of ultra-high molecular weight polypropylene is added to 100 parts by weight of ordinary polypropylene and extraction is performed in a temperature range above the melting point and below 210°C (Japanese Patent Announcement 61-28694 [1986]), extruded sheets comprised of two polypropylene components of an intrinsic viscosity ratio of 2 or greater and of different molecular weights obtained by a multiple stage polymerization method (Japanese Patent Announcement 1-12770 [1989]), a method in which polyethylene compositions comprised of three types of polyethylenes that contain 1 to 10 wt % of polyethylenes of high viscosity average molecular weights and that are of different high viscosity average molecular weights are manufactured by the melt kneading method or the multiple state polymerization method (Japanese Patent Disclosure No. 62-61057 [1987]), a method of polymerization by multiple stage polymerization using a high activity titanium-palladium solid catalyst component in which 0.05 up to 1 wt % of ultra-high molecular weight polyethylene of limiting viscosity of greater than 20 dl/g is polymerized (Japanese Patent Announcement 5-79683 [1993]) and a method of polymerization of polyethylene by multiple stage polymerization with a polymerization device having a special configuration using high activity titanium catalyst component that has been subjected to preliminary polymerization treatment with 1-butene or 4-methyl-1-pentene in which 0.1 to 5 wt % of ultra-high molecular weight polyethylene of an intrinsic viscosity greater than 15 dl/g is polymerized [Japanese Patent Announcement 7-8890 [1995]].

Other known methods include a method in which polypropylene having high melt tension is manufactured by polymerizing propylene using a preliminary polymerization catalyst in which ethylene and a polyene compound are subjected to preliminary polymerization in a supported solid catalyst component containing titanium and an organic aluminum compound catalyst (Japanese Patent Application Early Disclosure No. 5-222122 [1993]) and a method for manufacturing straight chain low-density polyethylene (LLDPE) having high melt tension in which preliminary polymerization is performed with ethylene alone using a similar catalyst component and in which a preliminary polymerization catalyst of a limiting viscosity greater than 20 dl/g is used (Japanese Patent Application Early Disclosure No. 4-55410 [1992]).

Attempts to improve melt tension when metallocene catalyst systems are used that have been proposed include methods in which a catalyst comprised of a silica carrier containing more than 1.0 wt % of water, metallocene, methyl aluminoxane and triisobutyl aluminum is used (Japanese Patent Application Early Disclosure No. 5-140224 [1993] and Japanese Patent Application Early Disclosure No. 5-140224 [1993]), a method in which two or more metallocenes are used as catalyst components [Japanese Patent Application Early Disclosure No. 5-255436 [1993], Japanese Patent Application Early Disclosure No. 5-255437 [1993] and Japanese Patent Application Early Disclosure No. 6-

206939 [1994]) and a method in which montmorillonite is used in a metallocene catalyst system (Japanese Patent Application Early Disclosure No. 7-188317 [1995]) and Japanese Patent Application Early Disclosure No. 7-188336 [1995]).

Although improvement in melt tension of polypropylene has been found to a certain degree under determination conditions of 190°C with various compositions and methods of manufacture using conventional catalyst systems, there are points that remain to be improved in respect to improving melt tension under conditions of use over 200°C, retention of bromine due to the auxiliary cross-linking agent, crystallization temperature and thermal stability of properties in addition to melt tension.

Further, although improvement in the melt tension of polypropylene at determination conditions of 190°C has been found to a certain degree in metallocene catalyst systems by the methods described above, melt tension is not necessarily satisfactory at temperatures higher than this, for example under use conditions greater than 200°, and improvement is desired.

Most recently, there have been reports of cases of copolymers such as unconjugated dienes and propylene using metallocene catalysts. For example, there are Japanese Patent Application Early Disclosure No. 5-222251 [1993] and Japanese Patent Application Early Disclosure No. 5-222121 [1993]. However, because there are no instances in which metallocene catalysts were used in the examples in these cases, the effects when metallocene catalysts are used cannot be presumed. The propylene copolymers that were obtained by polymerization above 45°C, which are practical polymerization temperatures, using the metallocene catalysts used in these cases exhibited low stereoregularity and were not of sufficient molecular weight. In addition, their melt tension was not sufficient, for which reason they could not be applied to practical uses.

Further, a case of copolymerization of propylene and ethylene with α,ω -dienes is reported in Japanese Patent Application Early Disclosure No. 7-138327 [1995]. However, the polymerization temperature is lower than a polymerization temperature greater than 45°C, which is the practical polymerization temperature, and the molecular weights of the copolymers that are obtained are extremely low. Moreover, because the catalyst system is not supported by a carrier, mass production by practical processes is difficult.

A case of copolymerization of propylene and polyvalent ene [sic] is reported in Japanese Patent Application Early Disclosure No. 8-92317 [1996]. However, the polymerization temperature is lower than a polymerization temperature over 45°, which is the practical polymerization temperature. In addition, although the stereoregularity of the polymers that were obtained was high at the polymerization temperature of 250°C indicated in the examples, it was low at polymerization temperatures above 45°C. Moreover, the proportion of units of irregular position on the basis of 2,1-insertions of propylene monomers among the total propylene insertions was greater than 1.0% so that it is difficult to say that there was a high degree of control of stereoregularity. Because

the catalyst system is not supported on a carrier, mass production by practical processes is difficult.

Further, the thermal stability of the copolymers of α,ω -dienes and propylene when the metallocene catalyst systems described above are used is not completely disclosed.

Accordingly, the objective of this invention is to provide a propylene copolymer and a method for its manufacture using a specific metallocene catalyst, which copolymer has high stereoregularity at practical polymerization temperatures, whereby the quantity of heterogeneous bonds in the polymer is controlled to a high degree, which has a narrow molecular weight distribution, a high melt tension, heat stability, a low MFR and excellent particle properties.

Disclosure of the Invention

The major characteristic of this invention, which was proposed in order to achieve the aforementioned objectives, is to polymerize propylene and a small quantity of α,ω -diene using a specified catalyst.

Specifically, this invention provides a propylene copolymer the melting point of which is 147°C to 160°C, the proportion of units of irregular position on the basis of 2,1 insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0% and the principle component of which is a random copolymer of propylene and α,ω -diene of Mw/Mn 1.5 to 3.8 which contains 0.01 to 2 wt % of α,ω -diene.

This invention further provides a propylene copolymer as described above the melting point of which is 152°C to 160°C.

This invention further provides a propylene copolymer the melting point of which is 100°C to 160°C, the proportion of units of irregular position in which on the basis of 2,1-insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0%, the principle component of which is a random copolymer of propylene that contains 0.01 to 2 wt % of α,ω -diene and that contains, at the same time, ethylene of Mw/Mn 1.5 to 3.8 or 0.1 to 15 wt % of α -olefin having 4 or more carbon atoms or ethylene and an α -olefin having 4 or more carbon atoms.

This invention further provides a propylene copolymer the proportion of units of irregular position in which on the basis of 2,1-insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0% and that contains 0.01 to 2 wt % of α,ω -diene, in the first step, a propylene random copolymer being polymerized that contains, at the same time, 0.1 to 15 wt % of homopropylene or ethylene, α -olefin having 4 or more carbon atoms or ethylene and an α -olefin having 4 or more carbon atoms, after which, in the second step, 30 to 80 wt % of propylene or ethylene or an α -olefin having four or more carbon atoms are successively or ethylene or an α -olefin having 4 or more carbon atoms are simultaneous copolymerized, , 5 to 70 wt % of the rubber component that is

obtained being polymerized and the propylene block copolymer that is obtained being randomly copolymerized as the principal component with the α,ω -diene in one step and/or two steps.

This invention further provides a propylene co-polymer as described above in which the α -olefin is at least one substance selected from a group comprised of 1-butene, 1 hexane and 1-octane.

This invention further provides a propylene copolymer as described above in which the α,ω -diene is at least one substance selected from 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene.

This invention further provides a propylene copolymer as described above in which the α,ω -diene is 1,9-decadiene.

This invention further provides a propylene copolymer as described above in which the α,ω -diene content is greater than 0.01 wt % and less than 0.05 wt %.

This invention further provides a method for the manufacture of the aforementioned propylene copolymer characterized in polymerization is carried out at a temperature greater than 45°C using a catalyst system of which the principal components are compounds (A), (B), (C) and (D) as described below.

Compound (A): A transition metal compound represented by general formula [I] below



[Wherein, $(C_5H_{4-m}R^1m)$ and $(C_5H_{4-n}R^2n)$ indicate cyclopentadienyl groups and m and n are integers of 1 to 3. R1 and R2 are hydrocarbon groups or silicon-containing hydrocarbon groups having 1 to 20 carbon atoms which may be the same or different. The position and type of R^1 and R^2 on the cyclopentadienyl ring assumes the position in which a symmetric face containing M is not present. R^1 or R^2 is present in at least one of the cyclopentadienyl rings and on at least one carbon atom that is adjacent to the carbon atoms that is bonded to Q. Q is a divalent hydrocarbon group, an unsubstituted silylene group or a hydrocarbon substituted silylene group that cross links with $(C_5H_{4-m}R^1m)$ and $(C_5H_{4-n}R^2n)$. M indicates a transition metal including titanium, zirconium or hafnium and X and Y, which may be the same or different, indicate hydrogen, halogens or hydrocarbon groups.

Compound (B): Aluminoxane

Compound (C): An organoaluminum compound

Compound (D): A particulate carrier

This invention provides a method for the manufacture of a propylene copolymer as described above in which compound (A) is dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) zirconium dichloride or dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) hafnium dichloride.

This invention further provides a method for the manufacture of the aforementioned propylene copolymer in which it is manufactured using a gaseous phase polymerization process.

Brief Explanation of the Figure

Figure 1 is a flow sheet of the method of manufacture of the propylene copolymer of this invention/

Optimum Mode for Executing the Invention

The major characteristic of this invention is that the propylene copolymer is polymerized at a temperature greater than 45°C using a supported catalyst system in which a specified metallocene compound is used.

The propylene copolymer that is obtained by this method is a copolymer of high stereoregularity of which the melting point is 147° to 160°C, and, preferably, 152°C to 160°C.

The supported catalyst system of this invention has as its principal components Compounds (A), (B), (C) and (D) as described below.

Compound (A): A transition metal compound represented by general formula [I] below



[Wherein, $(C_5H_{4-m}R^1m)$ and $(C_5H_{4-n}R^2n)$ indicate cyclopentadienyl groups and m and n are integers of 1 to 3. R1 and R2 are hydrocarbon groups or silicon-containing hydrocarbon groups having 1 to 20 carbon atoms which may be the same or different. The position and type of R¹ and R² on the cyclopentadienyl ring assumes the position in which a symmetric face containing M is not present. R¹ or R² is present in at least one of the cyclopentadienyl rings and on at least one carbon atom that is adjacent to the carbon atoms that is bonded to Q. Q is a divalent hydrocarbon group, an unsubstituted silylene group or a hydrocarbon substituted silylene group that cross links with $(C_5H_{4-m}R^1m)$ and $(C_5H_{4-n}R^2n)$. M indicates a transition metal including titanium, zirconium or hafnium and X and Y, which may be the same or different, indicate hydrogen, halogens or hydrocarbon groups.

Compound (B): Aluminoxane

Compound (C): An organoaluminum compound

Compound (D): A particulate carrier

The propylene polymer or copolymer that is obtained by polymerization aqt a temperature of greater than 45°C using this supported catalyst system is defined as described in (1) through (3) below.

(1) A propylene copolymer the melting point of which is 147°C to 160°C, the proportion of units of irregular position on the basis of 2,1-insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0% and the principle component of which is a random copolymer of propylene and α,ω -diene of Mw/Mn 1.5 to 3.8 which contains 0.01 to 2 wt % of α,ω -diene.

(2) A propylene copolymer the melting point of which is 100°C to 160°C, the proportion of units of irregular position in which on the basis of 2,1-insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0%, the principle component of which is a random copolymer of propylene that contains 0.01 to 2 wt % of α,ω -diene and that contains, at the same time, ethylene of Mw/Mn 1.5 to 3.8 or 0.1 to 15 wt % of α -olefin having 4 or more carbon atoms or ethylene and an α -olefin having 4 or more carbon atoms.

(3) A propylene copolymer the proportion of units of irregular position in which on the basis of 2,1-insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0% and that contains 0.01 to 2 wt % of α,ω -diene, in the first step, a propylene random copolymer being polymerized that contains, at the same time, 0.1 to 15 wt % of homopropylene or ethylene, α -olefin having 4 or more carbon atoms or ethylene and an α -olefin having 4 or more carbon atoms, after which, in the second step, 30 to 80 wt % of propylene or ethylene or an α -olefin having four or more carbon atoms are successively or ethylene or an α -olefin having 4 or more carbon atoms are simultaneous colpolymerized, , 5 to 70 wt % of the rubber component that is obtained being polymerized and the propylene block copolymer that is obtained being randomly copolymerized as the principal component with the α,ω -diene in one step and/or two steps.

The α,ω -diene that is used in this invention may have a straight-chain structure or a branched chain structure as long as it is a diene compound that at the least has vinyl bonds in the α position and the ω position. It may also contain hetero-atoms or atomic groups such as oxygen, sulfur or boron. For example, it can be 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,13-tetradecadiene and divinylbenzene, preferably, 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene, and more preferably, 1,9-decadiene. The content of α,ω -diene should be 0.01 to 0.1 wt %. When the content is excessively

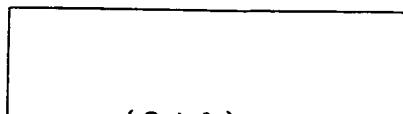
high, a gel component is produced. This is disadvantageous because fusion occurs again and cycling is difficult.

The α -olefin that is used in this invention can be 1-butene, 1-hexene, 2-octene, 1-decene, 4-methyl-1-pentene and styrene, and, preferably, 1-butene.

There are no particular limitations on the method of manufacture of the propylene copolymers (1) through (3) of this invention as long as the physical properties indicated above are satisfied. However, they can be manufactured preferably by polymerization at a temperature greater than 45°C using the supported catalyst system described above.

Compound (A) in the aforementioned supported catalyst system may be any compound as long as it is in the range described above. Examples include dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) titanium dichloride, dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) zirconium dichloride, dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) zirconium dimethyl, dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) hafnium dichloride, dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) hafnium dimethyl, dimethylsilylenebis (2-methyl,4-phenylindenyl) zirconium dichloride, dimethylsilylenebis (2-ethyl,4-phenylindenyl) zirconium dichloride, and, preferably, dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) zirconium dichloride.

Compound (B), aluminoxane, is an organoaluminum compound as represented by general formula [I] or [II] below.



[2]



Wherein, R³ is a hydrocarbon group having 1 to 6, and, preferably, 1 to 4, carbon atoms. Specific examples include alkyl groups such as a methyl group, an ethyl group, a propyl group, a butyl group, an isobutyl group, a pentyl group or a hexyl group, an alkenyl group such as an allyl group, a 2-methylallyl group, a propenyl group, an isopropenyl group, a 2-methyl-1-propenyl group or a butenyl group, a cycloalkyl group such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group or a cyclohexyl group and aryl groups. Of these, alkyl groups, in which R³ may be the same or different, are particularly desirable. Further, q is an integer of 4 to 30, preferably, of 6 to 30, and more preferably, of 8 to 30.

The aforementioned aluminoxanes can be prepared under various known conditions. Specifically, the following methods can be indicated.

- (1) A method in which a trialkyl aluminum is reacted directly with water using an organic solvent such as toluene or ether.
- (2) A method in which a trialkyl aluminum is reacted with a salt having water of crystallization such as, for example, copper sulfate hydrate or aluminum sulfate hydrate.
- (3) A method in which a trialkyl aluminum is reacted with water impregnated in silica gel.
- (4) A method in which trimethyl aluminum and isobutyl aluminum are mixed and in which the mixture is reacted directly with water using an organic solvent such as toluene or ether.
- (5) A method in which trimethyl aluminum and isobutyl aluminum are mixed and in which the mixture is reacted with a salt having water of crystallization such as, for example, copper sulfate hydrate or aluminum sulfate hydrate.
- (6) A method in which silica gel is impregnated with water and in which the water is reacted with triisobutyl aluminum, after which trimethyl aluminum is further reacted.

Example of Compound (C), the organoaluminum compound, include trialkyl aluminum compounds such as trimethyl aluminum, triethyl aluminum, triisopropyl aluminum, triisobutyl aluminum and tri-n-butyl aluminum, dialkyl aluminum halides such as dimethylaluminum chloride, dimethylaluminum bromide, diethylaluminum chloride and diisopropylaluminum chloride and alkyl aluminum sesquihalides such as methylaluminum sesquihalide, ethylaluminum sesquihalide and isopropylaluminum sesquihalide. One or more can be used.

Compound (D), the particulate carrier, may be an inorganic carrier or an organic carrier. Granular or spherical particulate solids of particle diameters of 1 to 500 µm, and, preferably, of 5 to 300 µm, are used.

Oxides are desirable as aforementioned particulate inorganic carriers. Specific examples can include SiO_2 , Al_2O_3 , MgO , ZrO_2 , TiO_2 or mixtures thereof. Of these, carriers having as their principal component at least one component selected from a group comprised of SiO_2 , Al_2O_3 and MgO are preferable. Said inorganic oxide carriers are ordinarily used after calcination at 100 to 1000°C for 1 to 40 hours. Instead of calcination, chemical dehydration methods by means of, for example, SiCl_4 or chlorosilane can be used. The inorganic compounds that are used for the carrier can be SiO_2 , Al_2O_3 , MgO , TiO_2 , ZnO or mixtures thereof, for example, $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-TiO}_2$ or $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$. Of these, those having SiO_2 or Al_2O_3 as the principal component are preferable.

Examples of the particulate organic carriers can include particulate organic carriers, for example, particulate copolymers of polyolefins such as polyethylene, polypropylene, poly-1-butene and poly-4-methyl-1-pentene and particulate polymers of polystyrene.

The catalyst systems that are used in this invention of which the principal components are compound (A), a metallocene, Compound (B), aluminoxane, compound (C), an organoaluminum compound, and compound (D), a particulate carrier are constituted having as their principal components a supported catalyst component having as its principal components compounds (A), (B) and (D) and a suitable compound (C) that is added separately to the reaction system at the time of polymerization as a scavenger.

The aforementioned supported catalyst component can be obtained suitably by reacting (A) and (B) in the presence of (D). Ordinarily, a hydrocarbon-soluble metallocene compound and aluminoxane are converted to the desired supported catalyst by precipitating said metallocene compound and aluminoxane onto a carrier that has been dehydrated.

The order in which the metallocene compound and the aluminoxane are added to the carrier can be varied as desired. For example, the metallocene compound, which has been dissolved in a suitable hydrocarbon solvent, can be added initially to the carrier, after which the aluminoxane can be added. In addition, the aluminoxane and the metallocene compound can be reacted in advance and the product can be added at the same time to the carrier. Further, the aluminoxane can be added initially, after which the metallocene compound can be added. The temperature during the reaction is ordinarily -20 to 100°C, and, preferably, 0 to 100°C, and the time required for the reaction should ordinarily be greater than 1 minute, and, preferably, in a range of 1 minute to 200 minutes. The supported catalyst, as required, can also be used after preliminary polymerization with a small quantity of olefin.

The olefins that are used for preliminary polymerization can include ethylene, propylene, 1-butene, 1-hexene, 3-methyl-1-butene and 4-methyl-1-pentene. Two or more monomers can be copolymerized.

The supported catalyst that has been prepared in this way can be used for propylene polymerization or copolymerization together with the organoaluminum compound (C), which is used as a scavenger.

Known propylene polymerization and copolymerization processes can be used as the method of polymerization of the propylene copolymers of this invention. The slurry polymerization method in which propylene is polymerized or copolymerized in aliphatic hydrocarbons such as butane, pentane, hexane, heptane or iso-octane, alicyclic hydrocarbons such as cyclopentane, cyclohexane or methyl cyclohexane, aromatic hydrocarbons such as toluene, xylene or ethyl benzene and inactive solvents such as gasoline fractions or hydrogenated diesel oil fraction, bulk polymerization in which the propylene monomer itself is used as the solvent, the gaseous phase polymerization method in which propylene polymerization or copolymerization is executed in the gaseous phase, solution polymerization in which the propylene polymer or copolymer that has been produced by polymerization or copolymerization is in the liquid state and polymerization processes in which two or more of these processes are combined can be used.

The polymerization conditions that can be used are polymerization conditions similar to those for polymerization or copolymerization of olefins by known Ziegler catalysts. Specifically, polymerization temperature is a temperature of 50 to 150°C, and, preferably, 50 to 100°C, polymerization pressure is atmospheric pressure to 7 Mpa, and, preferably, 0.1 Mpa to 5 Mpa, and polymerization time is ordinarily on the order for 1 minute to 20 hours. Molecular weight regulation of the propylene polymer or copolymer that is obtained is achieved by selection of polymerization conditions as described above, and, in addition, by inserting hydrogen, which is a molecular weight regulator, into the polymerization system.

After copolymerization has been completed, as required, the target propylene copolymer can be obtained after post-treatment processes such as known catalyst deactivation treatment processes, catalyst residue elimination processes and drying processes have been performed.

The intrinsic viscosity [η] of the propylene copolymer of this invention as determined in tetralin at 135°C is 0.2 to 10 dl/g.

The following relationship exists between the melt tension (MS) at 230°C and the melt flow index (MFR) determined at a load of 21.18 N and at 230°C of the propylene copolymer of this invention obtained as described above.

$$\log (\text{MS}) > -1.28 \times \log (\text{MFR}) + 0.44$$

Here, melt tension (MS) at 230°C is the value (unit: cN) determined for the tension of filamentous polypropylene composition using a Model 2 melt tension tester (manufactured by Toyo Seiki Seisakujo (Ltd.)) when the olefin polymer or copolymer composition is heated to 230°C in the device, the fused olefin polymer or copolymer

composition is extruded into the atmosphere at 23°C at a rate of 20 mm/minute from a nozzle of 2.095 mm in diameter to make a strand and the strand is withdrawn at a rate of 3.14 m/minute.

The proportion of units or irregular position on the basis of the 2,1-insertions of the propylene monomer in the total propylene insertions in the propylene copolymer of this invention is 0.05 to 1.0%.

The proportion of units of irregular position on the basis of 2,1-insertions is found using ^{13}C -NMR by reference to Polymer 30, 1350 (1989).

The α,ω -diene content can be found by calculation using ^{13}C -NMR as described in Japanese Patent Application Early Disclosure No. 7-138327 [1995] and in Japanese Patent Application Early Disclosure No. 8-92317 [1996] and can also be found from the difference between the number of moles of diene monomer supplied during polymerization and the number of moles of unreacted diene monomer at the time polymerization has been completed.

Various additives such as antioxidants, ultraviolet ray absorbents, antistatic agents, nucleating agents, lubricants, flame retardants, anti-blocking agents, colorants and inorganic or organic fillers as well as various synthetic resins can be compounded with the propylene copolymers of this invention in ranges that do not impair the objectives of this invention. Ordinarily, they are supplied for the manufacture of various molded products in pellet state in which they are heated, fused and kneaded and further cut to particle shape.

Examples

We shall now describe this invention in further detail by means of examples and comparative examples.

The definitions of the terminology that is used on the examples and comparative examples and the methods of determination are as described below.

MFR: The value determined in accordance with JIS K7210 by condition 14 in Table 1 (at a load of 21.18 N and at 230°C (unit: g/10 minutes)).

Intrinsic viscosity [η]: Value obtained by determining intrinsic viscosity determined in tetralin at 135°C with an Ostwald's viscometer (manufactured Mitsui Toatsu Chemicals (Ltd.)) (unit: dl/g).

Melt flow rate (MFR): Value determined in accordance with JIS K7210 by condition 14 of Table 1 (at a load of 21.18 and at 230°C (unit: g/10 minutes))

Melt tension (MS): Value determined with a Model 2 melt tension tester (manufactured by Toyo Seiki Seisakujo) (unit: cN)

Melting point (Tm): A model DSC7 differential scanning calorimeter (manufactured by Perkins-Elmer) was used. The temperature of the olefin polymer or copolymer was raised from room temperature to 230°C at a temperature elevation rate of 30°C/minute and the material was maintained at this temperature for 10 minutes, after which the temperature was lowered to -20°C at -20°C/minute and the material was maintained at this temperature for 10 minutes. Following that, the temperature at which a peak during fusion was shown under temperature elevation conditions of 20°C/minute was taken as the melting point.

Crystallization temperature (Tc): A model DSC7 differential scanning calorimeter (manufactured by Perkins-Elmer) was used. The temperature of the olefin polymer or copolymer was raised from room temperature to 230°C at a temperature elevation rate of 30°C/minute and the material was maintained at this temperature for 10 minutes, after which the temperature was lowered to -20°C at -20°C/minute and the material was maintained at this temperature for 10 minutes. Following that, the temperature was raised to 230°C at a temperature elevation rate of 20°C/minute and the material was maintained at the temperature for 10 minutes, after which was lowered to 150°C at -80°C/minute. Crystallization temperature (unit: °C) was the temperature at which the maximum peak during crystallization was shown as the temperature was lowered from 150°C at -5°C/minute.

Molecular weight distribution (Mw/Mn): Mw, Mn and Mw/Mn were calculated on the basis of the results of determinations by gel permeation chromatography in accordance with the following methods. Specifically, they were found by determinations at 135°C using an o-dichlorobenzene solution of a concentration of polymer of 0.05 wt % and using a mixed polystyrene gel column (for example, a PSK gel GMHS-HT manufactured by Toso (Ltd.)). The determination apparatus used was, for example, a GPC-150C manufactured by the Waters Company.

Thermal stability: 0.1 parts by weight of 2,6-di-t-butyl-p-cresol and 0.1 parts by weight of potassium stearate were mixed per 100 parts by weight of propylene copolymer, the mixture was fused, kneaded and pelletized at 230°C using an extrusion pelletizing machine of a screw diameter of 40 mm and pellets of propylene copolymer were prepared.

Thermal stability was assessed in the following way. The melt flow ratyes (MFR) (unit: g/10 minutes) of the pellets that were obtained as described above and of pellets that were finally obtained by repeating fusion, kneading and pelletization two times using

the aforementioned extrusion pelletizing machine were determined in accordance with condition 14 in Table 1 of JIS K7210 and the difference between final MFR of the pellets and the MFR of the pellets obtained initially (final pellet MFR – initial pellet MFR = Δ MFR) was calculated. A lower difference (Δ MFR) indicates better thermal stability.

Example 1

[Preparation of supported carrier]

0.39 g (0.889 mmol) of dimethylsilylene (2,3,5-trimethylcyclopentadienyl) (2',4',5'-trimethylcyclopentadienyl) zirconium dichloride and 267 mmol of a toluene dilution of methyl aluminoxane converted as Al atoms were added to a 500 ml flask that had been thoroughly dried and the atmosphere of which had been replaced with N₂ and a reaction was carried out for 10 minutes. Following that, 10 g of silica (Grace Davison [phonetic]) that had been calcinated for 8 hours at 800°C was added and the mixture was stirred for 10 minutes. As a vacuum was being applied from the top of the vessel, a slight flow of N₂ was added from the bottom. The mixture was heated at 70°C for 9 hours as the solvent was being evaporated. The dried solid was cooled overnight to room temperature. The solid catalyst that was obtained in this way and 250 ml of isopentane was added to a 500 ml flask that had been thoroughly dried and the atmosphere of which had been replaced with N₂ and the mixture was cooled to 0°C.

Ethylene was then added continuously for 4 hours at a flow rate of 80 ml/minute and preliminary polymerization was performed. Following that, the supernatant was decanted and decantation and washing were performed 4 times with 100 ml of isopentane. Vacuum drying was then carried out for 2 hours at room temperature, with 35 g of supported catalyst being prepared.

[Manufacture of propylene copolymer]

12 mmol of triethyl aluminum was added to a 15L autoclave the atmosphere of which had been thoroughly replaced with N₂ and 2 g (14.5 mmol) of 1,9-decadiene was added. 8L of liquefied propylene was then added, the temperature was raised to 50°C and the mixture was stirred for 10 minutes. 2.18 g of the supported catalyst that had been prepared as described above as a hexane slurry was introduced under pressure as washing was being performed with 2L of liquefied propylene, by which means polymerization was initiated. Polymerization was then performed for 2 hours at 50°C. 1.8 Kg of powder was obtained. When the copolymer of propylene and 1,9-decadiene that was obtained in this way was analyzed, the melting point was 155.8°C, the crystallization temperature was 114.8°C, the 1,9-decadiene content was 0.01 wt %, the proportion of units of irregular position based on the 2,1-insertions of propylene monomer in the total insertions was 0.4% and melt tension was 0.6 cN. MFR was 9.5 g/10 minutes and Mw/Mn was 2.5. Density was 0.43 g/ml.

[Evaluation of thermal stability]

The initial pellet MFR was 9.5 g/10 minutes and the final pellet MFR was 9.7 g/10 minutes. As a result, Δ MFR was 0.2. Thus, thermal stability was extremely good.

Example 2

[Manufacture of propylene copolymer]

12 mmol of triethyl aluminum was added to a 15L autoclave the atmosphere of which had been thoroughly replaced with N₂ and 3.4 g (24.6 mmol) of 1,9-decadiene was added. 8L of liquefied propylene was then added, the temperature was raised to 50°C and the mixture was stirred for 10 minutes. 2.1 g of the supported catalyst that had been prepared in Example 1 as a hexane slurry was introduced under pressure as washing was being performed with 2L of liquefied propylene, by which means polymerization was initiated. Polymerization was then performed for 2 hours at 50°C. 1.9 Kg of powder was obtained. When the copolymer of propylene and 1,9-decadiene that was obtained in this way was analyzed, the melting point was 156.6°C, the crystallization temperature was 114.9°C, the 1,9-decadiene content was 0.02 wt %, the proportion of units of irregular position based on the 2,1-insertions of propylene monomer in the total insertions was 0.4% and melt tension was 7.5 cN. MFR was 1.0 g/10 minutes and Mw/Mn was 2.6. Density was 0.43 g/ml.

Comparative Example 1

[Preparation of supported carrier]

The supported carrier was prepared in the same way as in Example 1 except that dimethylsilylene bis(2-methyl,4,5-benzoindenyl) zirconium dichloride was used instead of (2,3,5-trimethylcyclopentadienyl) (2',4',5'-trimethylcyclopentadienyl) zirconium dichloride as the metallocene.

[Preparation of propylene copolymer]

12 mmol of triethyl aluminum was added to a 15L autoclave the atmosphere of which had been thoroughly replaced with N₂ and 2.0 g (14.5 mmol) of 1,9-decadiene was added. 8L of liquefied propylene was then added, the temperature was raised to 50°C and the mixture was stirred for 10 minutes. 2.0 g of the supported catalyst that had been prepared as described above as a hexane slurry was introduced under pressure as washing was being performed with 2L of liquefied propylene, by which means polymerization was initiated. Polymerization was then performed for 2 hours at 50°C. 2.0 Kg of powder was obtained. When the copolymer of propylene and 1,9-decadiene that was obtained in this way was analyzed, the melting point was 144.2°C, the crystallization temperature was 106.7°C, the 1,9-decadiene content was 0.01 wt %, the proportion of units of irregular position based on the 2,1-insertions of propylene monomer in the total insertions was 1.6% and melt tension was 5.9 cN. MFR was 1.1 g/10 minutes and Mw/Mn was 2.7. Density was 0.40 g/ml.

Comparative Example 2

[Preparation of propylene copolymer]

8L of liquefied propylene was added to a 15L autoclave the atmosphere of which had been thoroughly replaced with N₂, the temperature was raised to 50°C and the mixture was stirred for 10 minutes. 2.3 g of the supported catalyst that had been prepared in Example 1 as a hexane slurry was introduced under pressure as washing was being performed with 2L of liquefied propylene, by which means polymerization was initiated. Polymerization was then performed for 2 hours at 50°C. 0.6 Kg of powder was obtained. The melt tension of the propylene polymer that was obtained in this way was 0.2 cN. MFR was 9.6 g/10 minutes and Mw/Mn was 2.4. Density was 0.40 g/ml.

As should be clear from a comparison of the foregoing examples and comparative examples, when a supported carrier other than the specified metallocene compounds of this invention was used, a product of superior melt tension and molecular weight could not be obtained at polymerization temperatures greater than 45°C.

Industrial Usefulness

Propylene copolymers having high stereoregularity, in which the quantity of heterogeneous bonds in the polymer can be controlled to a high degree, having a narrow molecular weight distribution, high melt tension, thermal stability, a low MFR and excellent particle properties can be obtained at practical polymerization temperatures using the specified metallocene catalyst system of this invention.

Claims

(1) A propylene copolymer the melting point of which is 147°C to 160°C, the proportion of units of irregular position on the basis of 2,1-insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0% and the principle component of which is a random copolymer of propylene and α,ω -diene of Mw/Mn 1.5 to 3.8 which contains 0.01 to 2 wt % of α,ω -diene.

(2) A propylene copolymer as described in Claim 1 the melting point of which is 152°C to 160°C.

(3) A propylene copolymer the melting point of which is 100°C to 160°C, the proportion of units of irregular position in which on the basis of 2,1-insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0%, the principle component of which is a random copolymer of propylene that contains 0.01 to 2 wt % of α,ω -diene and that contains, at the same time, ethylene of Mw/Mn 1.5 to 3.8 or 0.1 to 15 wt % of α -olefin having 4 or more carbon atoms or ethylene and an α -olefin having 4 or more carbon atoms.

(4) A propylene copolymer the proportion of units of irregular position in which on the basis of 2,1-insertions of propylene monomer in the total propylene insertions is 0.05 to 1.0% and that contains 0.01 to 2 wt % of α,ω -diene, in the first step, a propylene random copolymer being polymerized that contains, at the same time, 0.1 to 15 wt % of homopropylene or ethylene, α -olefin having 4 or more carbon atoms or ethylene and an α -olefin having 4 or more carbon atoms, after which, in the second step, 30 to 80 wt % of propylene or ethylene or an α -olefin having four or more carbon atoms are successively or ethylene or an α -olefin having 4 or more carbon atoms are simultaneous copolymerized, .5 to 70 wt % of the rubber component that is obtained being polymerized and the propylene block copolymer that is obtained being randomly copolymerized as the principal component with the α,ω -diene in one step and/or two steps.

(5) A propylene co-polymer as described in Claims 2 or 3 in which the α -olefin is at least one substance selected from a group comprised of 1-butene, 1-hexane and 1-octane.

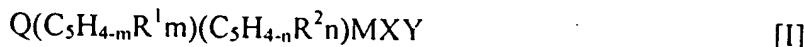
(6) A propylene copolymer as described in any one of Claims 1 through 4 in which the α,ω -diene is at least one substance selected from 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene.

(7) A propylene copolymer as described in any one of Claims 1 through 4 in which the α,ω -diene is 1,9-decadiene.

(8) A propylene copolymer as described in any one of Claims 1 through 6 in which the α,ω -diene content is greater than 0.01 wt % and less than 0.05 wt %.

(9) A method for the manufacture of the aforementioned propylene copolymer as described in any one of Claims 1 through 8 characterized in that polymerization is carried out at a temperature greater than 45°C using a catalyst system of which the principal components are compounds (A), (B), (C) and (D) as described below.

Compound (A): A transition metal compound represented by general formula [I] below



[Wherein, $(C_5H_{4-m}R^1m)$ and $(C_5H_{4-n}R^2n)$ indicate cyclopentadienyl groups and m and n are integers of 1 to 3. R1 and R2 are hydrocarbon groups or silicon-containing hydrocarbon groups having 1 to 20 carbon atoms which may be the same or different. The position and type of R^1 and R^2 on the cyclopentadienyl ring assumes the position in which a symmetric face containing M is not present. R^1 or R^2 is present in at least one of the cyclopentadienyl rings and on at least one carbon atom that is adjacent to the carbon atoms that is bonded to Q. Q is a divalent hydrocarbon group, an unsubstituted silylene group or a hydrocarbon substituted silylene group that cross links with $(C_5H_{4-m}R^1m)$ and $(C_5H_{4-n}R^2n)$. M indicates a transition metal including titanium, zirconium or hafnium and X and Y, which may be the same or different, indicate hydrogen, halogens or hydrocarbon groups.

Compound (B): Aluminoxane

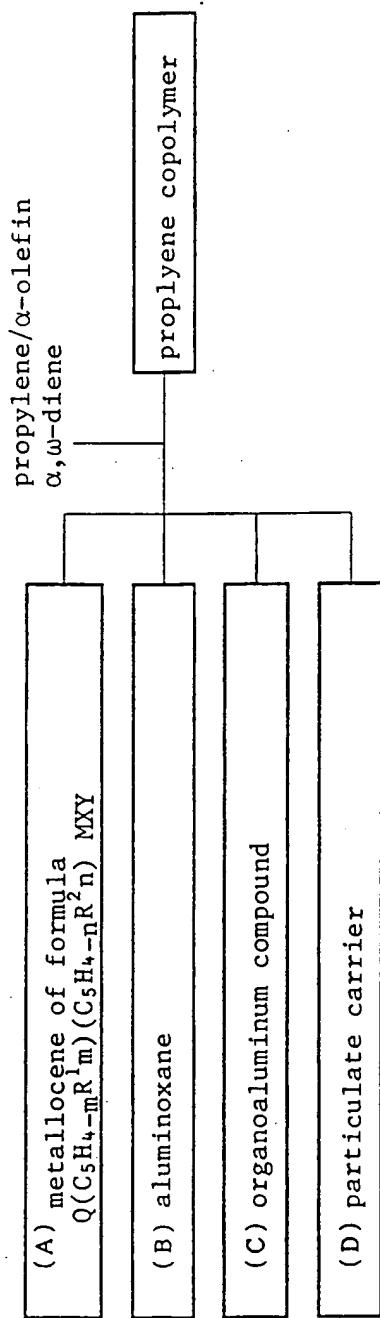
Compound (C): An organoaluminum compound

Compound (D): A particulate carrier

(10) A method for the manufacture of a propylene copolymer as described in Claim 8 in which compound (A) is dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) zirconium dichloride or dimethylsilylene (2,3,5-trimethylcyclopentadienyl)(2',4',5'-trimethylcyclopentadienyl) hafnium dichloride.

(11) A method for the manufacture of the aforementioned propylene copolymer as described in Claims 9 or 10 in which it is manufactured using a gaseous phase polymerization process.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/03945

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl' C08F210/06, C08F297/08, C08F4/642

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl' C08F10/00-10/14, 210/00-210/18, 297/06-297/08, 4/60-4/70

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 07-138327, A (Mitsui Toatsu Chemicals, Inc.), 30 May, 1995 (30. 05. 95), Claims ; Par. Nos. [0041] to [0047] (Family: none)	1-11
A	JP, 08-092317, A (Showa Denko K.K.), 9 April, 1996 (09. 04. 96), Claims ; Par. Nos. [0026] to [0046] (Family: none)	1-11
A	JP, 07-165814, A (Mitsui Toatsu Chemicals, Inc.), 27 June, 1995 (27. 06. 95), Claims ; Par. Nos. [0039] to [0047] (Family: none)	1-11
A	JP, 04-025514, A (Mitsui Toatsu Chemicals, Inc.), 29 January, 1992 (29. 01. 92), Claims ; page 4, lower left column, line 14 to page 5, lower left column, line 14 & EP, 476148, A & US, 5219968, A & DE, 69112322, E	1-11

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 30 September, 1998 (30. 09. 98)	Date of mailing of the international search report 13 October, 1998 (13. 10. 98)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.